NASA CR-112003

THE DEVELOPMENT OF AUTOCLAVE PROCESSABLE, THERMALLY STABLE ADHESIVES FOR TITANIUM ALLOY AND GRAPHITE COMPOSITE STRUCTURES

BY

R. W. VAUGHAN AND R. J. JONES

DECEMBER 1971

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

PREPARED UNDER CONTRACT NO. NAS1-9532 BY

TRW
SYSTEMS GROUP

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FOREWORD

This document is the final report for the work performed during the period 7 September 1970 through 7 September 1971 by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-9532. The report covers Tasks IV, V, VI, VII and VIII of the program which involves Development of Autoclave Processable Thermally Stable Adhesives for Titanium Alloy and Graphite Composite Structures. A report covering Tasks I, II and III of the program which involved the Development of Thermally Stable Adhesives for Titanium Alloy and Boron Composite Structures was issued as NASA Contractor Report CR-1824 in July 1971.

This work was conducted under the technical direction of Mr. Robert Baucom of the Langley Research Center, Hampton, Virginia.

The Applied Chemistry Department of the Chemistry and Chemical Engineering Laboratory, Applied Technology Division were responsible for the work performed on this program. Dr. E. A. Burns, Manager, Applied Chemistry Department, provided overall program supervision and Mr. R. W. Vaughan, Product Development Section, was Program Manager. Major technical contributions throughout the program were provided by Mr. J. F. Creedon, adhesive formulary and evaluation; Mr. K. K. Ueda, adhesive processing; Dr. R. J. Jones, polymer synthesis and Mr. G. Fukumoto, structural testing.

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THE DEVELOPMENT OF AUTOCLAVE PROCESSABLE, THERMALLY STABLE ADHESIVES FOR TITANIUM ALLOY AND GRAPHITE COMPOSITE STRUCTURES

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1. INTRODUCTION AND SUMMARY

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center under the second phase of Contract NAS1-9532 during the period 7 September 1970 through 7 September 1971. The objective of this work was to develop an autoclave processable, thermally stable adhesive for bonding titanium alloy and graphite composite substrates.

Previous work under the first phase of this contract successfully provided a thermally stable adhesive suitable for press-bonding titanium alloy and boron composite substrates (Reference 1). Technology developed during this earlier phase employed the copolymeric blending of an A-type polyimide amide-acid (P11B) with an amide-imide amide-acid (Amoco AI-1137). This resin system was filled with aluminum powder and a thixotropic agent (Cab-O-Sil) was added to provide an adhesive formulation. Lap-shear and short beam shear specimens were press-bonded and tested at selected temperatures, *i.e.*, -65°F, 70°F and 600°F. Strengths obtained were superior to values reported for bonded joints utilizing other commercially available adhesive systems.

Autoclave processability of TRW A-type polyimide resins for advanced composites was demonstrated under Contract F33615-70-C01392 (Reference 2) and Contract NAS3-13489 (Reference 3). Basic technology developed during these two programs employed the modification of A-type polyimide formulations containing a single diamine (P13N and P10P) by use of a mixed diamine formulation wherein thio-dianiline (TDA) was one of the two diamines (P10SA and P10PA). This same approach was used successfully to modify the P11B resin formulation during the second phase of this contract. The autoclave processable A-type polyimide adhesive resin developed during this second phase was termed P11BA

and was substituted for P11B resin to prepare autoclavable adhesive formulations. Properties of adhesive joints bonded by autoclave processing exceeded the values obtained from press-bonded joints during the first phase (Reference 1). Also, an additional feature observed was that the short beam shear strength of autoclave molded Courtaulds HTS high strength graphite fiber reinforced P11BA resin composites was higher than that obtained during a previous program (Reference 2) with the same reinforcement and P105A resin.

The second phase of the program consisted of five basic tasks:

TASK IV - EVALUATION AND PREPARATION OF RESINS AND ADHESIVES

TASK V - DEVELOPMENT OF AUTOCLAVE BONDING PROCESS

TASK VI - PREPARATION OF EVALUATION SPECIMENS

TASK VII - EVALUATION TESTS

TASK VIII- ADHESIVE FILM OPTIMIZATION AND EVALUATION

The Task VIII Adhesive Film Optimization and Evaluation Task was added to the contract in order to investigate methods of reproducibly controlling bondline thickness of press-bonded joints. Because technology developed during this effort was going to be equally applicable to autoclave bonded joints, this task therefore was performed first and consequently is reported in Section 2 of this document. Sections 3, 4 and 5 discuss sequentially Resin Evaluation, Process Development and Evaluation Tests. Conclusions were drawn from the results of this effort and are listed together with recommendations for related studies which warrant further investigation. Significant experimental details supplementing the narrative of this report are provided in the Appendices.

2. ADHESIVE FILM OPTIMIZATION AND EVALUATION

A study was performed to determine the lap shear strength of specimens prepared with AlP paste adhesive on various glass fabrics and scrims, and to determine the reproducibility of the bondline thickness for the optimum adhesive film and process. Additional studies were completed showing that short post-cure cycles considerably improved both ambient and elevated temperature lap shear strengths of the specimens. Details of these studies are given in the following text.

2.1 PREPARATION OF ADHESIVE FILMS

Adhesive paste AlP was prepared in accordance with the procedures described in Appendix B and then was coated onto various types of glass fiber carriers which were selected to provide variations in both bondline thickness and glass fiber content. Wiper bars were used to control the thickness of the adhesive coating on the glass fiber carriers after which the films were dried partially in an air circulating oven for 5 minutes at 250°F. The resultant films possessed excellent drapability and slight tack. (Tackiness of these films was increased during assembly operations by the application of local heat and pressure, *i.e.*, with a warm lay-up iron.)

2.2 EVALUATION OF ADHESIVE FILMS

Titanium alloy 6Al-4V lap-shear panels (See Appendix C, Figure C2) were prepared for bonding by cleaning and then priming with adhesive Primer P2 in accordance with the procedures described in Appendix D2. The adhesive film then was laid onto the mating surfaces and imidized in an air circulating oven for the cycle prescribed in Table I. These panels were press-bonded under 100 psig pressure at 600°F for 60 minutes cure cycle followed by an oven post-cure of 16 hours at 550°F.

An oven post-cure was used because the results from brief post-cure studies showed improved shear strengths. These studies consisted of testing 6Al-4V titanium alloy lap shear specimens bonded with AlP adhesive at room temperature before and after post-cure. Details of the test specimens bonding procedures and the resultant lap shear strengths are provided in Table II. It was concluded from these data that a post-cure cycle noticeably improves the shear strength of AlP adhesive.

TABLE I. EFFECT OF GLASS FIBER CARRIERS AS ADHESIVE[a] SUPPORT ON LAP SHEAR STRENGTH[b]

Glass Fabric Support System	Resin Content[c] %	Bondline Thickness Mils	Tensile Lap Shear Strength (psi)			
			At Room Temperature	Standard Deviation	At 600°F After 10 Min. Soak	Standard Deviation
Style 181/A1100 Finish	23.9	0.0190	3050	289	2110	156
Style 1562/Volan Finish	27.6	0.0111	2950	185	2090	14
Style 112/A1100 Finish	--	0.0112	3146	189	2060	141
Style 104/A1100 Finish	31.8	0.0092	3533	306	2250	99
Style 1562/ Finish Removed	30.1	0.0104	3293	129	1940	113
Style 104/ Finish Removed	31.8	0.0099	3053	220	1890	7
Style 104/A1100 Finish (d)	31.8	0.0094	3900	211	2170	156

(a) Adhesive and primer formulation per Appendix B using P11B resin.

(b) All panels were bonded at 100 psig for 60 minutes at 600°F followed by a post cure of 16 hours at 550°F.

(c) Determined by resin burn-off at 1100°F after first removing volatiles by exposure to 550°F for 30 minutes.

(d) Adhesive film was imidized 5 minutes at 275°F and 5 minutes at 350°F while all the other specimens. received 5 minutes at 250°F only.

TABLE II.

POST-CURE STUDIES

Cure Cycle			Shear Strength, psi	
Minutes	°F	psig	Before Post-Cure	After Post-Cure[a]
60	550	100	1472	2800
45	600	150	2280	3600
60	600	100	2320	3186
60[b]	550	100	2720	4000

(a) 16 hours at 550°F in an air-circulating oven.

(b) Panel 180, prepared during Task II studies on 2 April 1970.

Further studies were performed in order to determine the effects of post-cure in an inert atmosphere. Two sets of titanium alloy 6Al-4V lap shear specimens were prepared and post-cured, one set for 16 hours at 550°F in air and the other set for 6 hours at 640°F in nitrogen. These then were tested after aging in air at 600°F for 0, 300 and 600 hours. The results (Figure 1) showed that there was no significant advantage in using an inert atmosphere/higher temperature post-cure over the cycle of 16 hours at 550°F in air.

The results presented in Table I show that Style 104/A1100 (amino-silane coupling agent) glass scrim provided the best lap shear strength at ambient and elevated temperature. Additional imidizing of the supported adhesive film for 15 minutes at 275°F and 5 minutes at 350°F improved the ambient temperature shear strength while the elevated temperature values remained essentially the same. Removal of the glass fiber finish by exposing the glass fabric to 1100°F for 3 hours before adhesive coating provided no improvement in shear strength for either the Style 1562 fabric or the 104 scrim. This Style 104 glass scrim supported adhesive film was shown to provide a bondline thickness in the range of 0.0092 to 0.0099-inch reproducibly, which apparently is close to optimum for this adhesive based on lap shear strength.

Therefore, adhesive film supported with Style 104/A1100 glass scrim (designated A1F) was selected for the preparation of evaluation specimens for delivery to NASA Langley Research Center. The imidizing cycle of 15 minutes at 275°F plus 5 minutes at 350°F also was selected for preparing these panels.

Employing the above adhesive film and process, a total of twenty-five lap shear panels (125 test coupons) were prepared. One test coupon from each panel was tested at room temperature in order to provide quality control on the panels. These tests showed that the room temperature lap shear strength range was 3000 psi to 3600 psi and the bondline thickness range was from 0.006 to 0.010-inch. Details of the strength and bondline thickness distribution are provided in Figures 2 and 3. The remaining test coupons (100) were sent to NASA Langley Research Center for further evaluation.

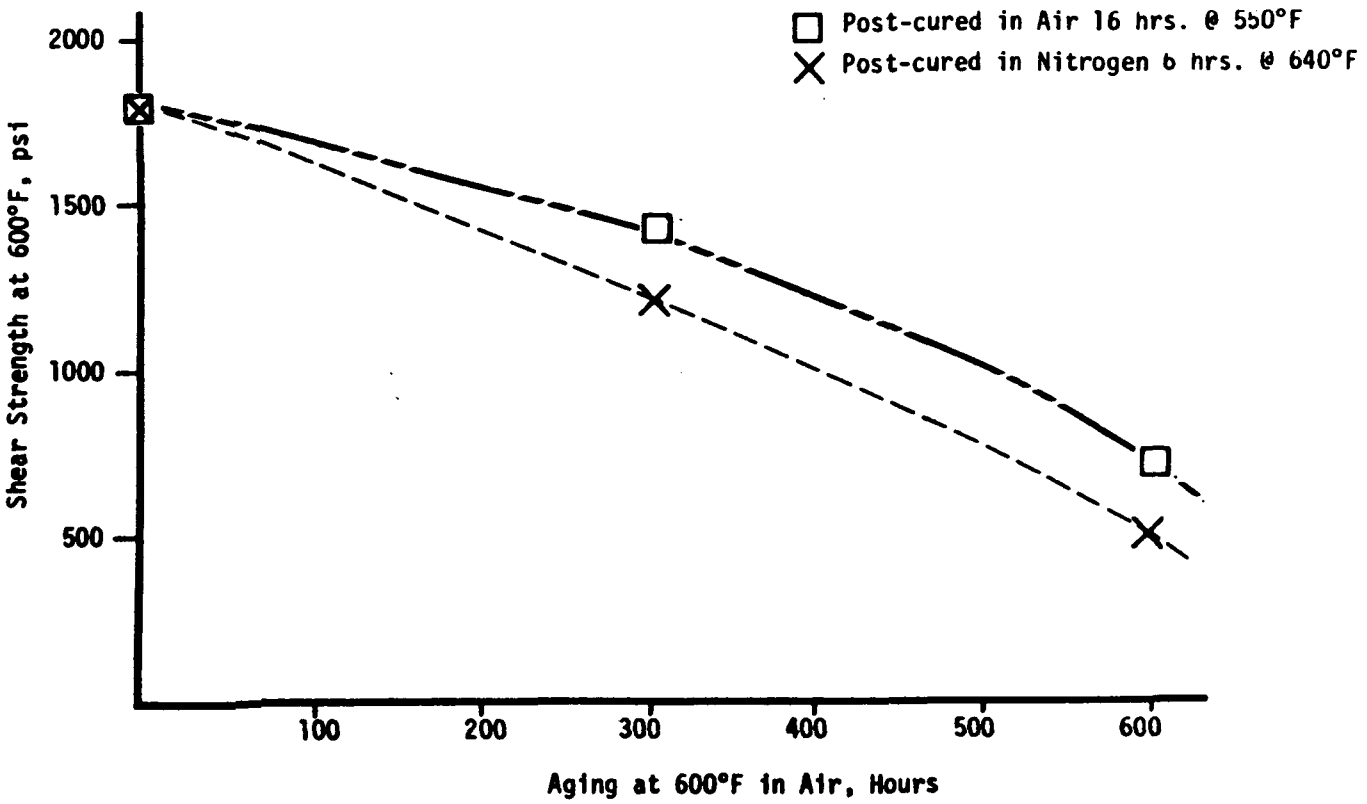


Figure 1. Inert Atmosphere Post-Cure Studies

3. EVALUATION OF RESINS FOR AUTOCLAVE PROCESSING

The utility of a specific A-type polyimide resin matrix, P11B, was demonstrated in the first phase of this contract during preparation of press-bonded structures. However, this particular formulation did not adapt to the processing requirements, such as high flow and slower cure rate, for autoclave processability. Consequently, as discussed below, P11B was modified in terms of ingredients, and screened for autoclave processability with other promising A-type polyimide formulations selected from other development programs.

3.1 SELECTION OF CANDIDATE RESINS

The A-type polyimide adhesive candidates screened for study are presented in Table III describing their code, ingredients and formulated molecular weight. The resins were prepared as amide-acid (A-A) prepolymers at a 40% w/w solids loading in dimethyl formamide (DMF) (See Appendix A). Each of the ingredients were purified before use to a level of >94% active functionality to ensure high quality prepolymer matrices for process screening studies.

3.2 RESIN SCREENING STUDIES

Primer and adhesive compounds were prepared from the six candidate A-type polyimide resins and from P11B resin (used as the control system). These compounds were prepared in the same manner as described in Appendix B for Primer P2 and Adhesive Paste A1P except that the candidate A-type polyimide formulations were substituted for P11B.

Lap-shear test specimens for the press bonding evaluations were prepared by the process described in Appendix D-4. Those specimens for simulated autoclave bonding evaluations were prepared similarly except the test coupon assembly was loaded into a cold press and 200 psig pressure was applied immediately. Cure temperature then was attained by slowly heating with the electrically heated press platens at the rate of 6-7°F/min up to cure temperature. These assemblies then were cured at 600°F for one hour while maintaining the 200 psig pressure and oven post-cured at 550°F for 16 hours without pressure. Lap shear strengths at room temperature and at 600°F after 10 minutes thermal soak were determined and are reported in Table IV.

Average (25 specimens), Ksi-3.34

Range, Ksi -3.00 to 3.60

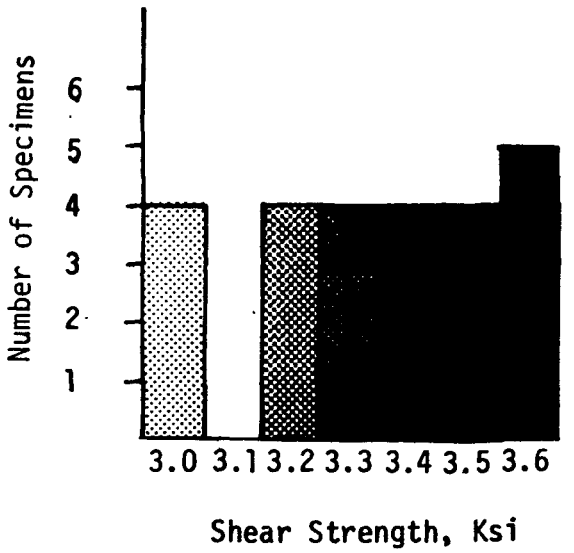


Figure 2. Shear Strength Property Distribution

Average (25 specimens), inch - 0.008

Range, inch - 0.006 to 0.010

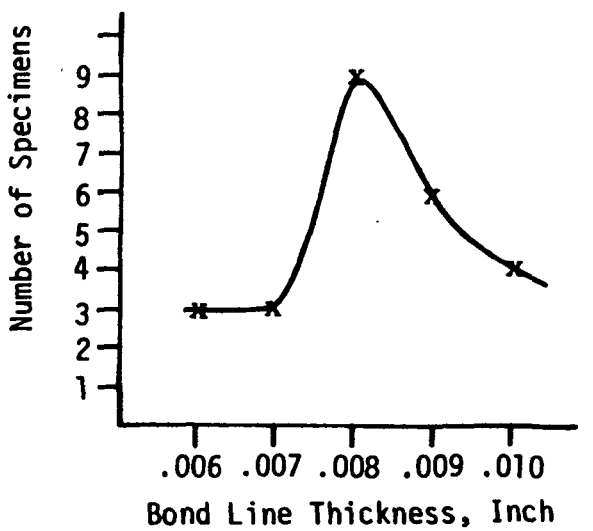


Figure 3. Bond-Line Thickness Distribution

TABLE III.

POLYIMIDE RESIN FORMULATIONS SCREENED FOR AUTOCLAVE PROCESSABILITY

Code	Ingredients Employed	Formulated Molecular Weight (g/mol)
P11B[a]	Nadic anhydride (NA)/*meta*-phenylene diamine (MPD)/benzophenone tetracarboxylic acid dianhydride (BTDA)	1100
P10PA[b]	Methyl nadic anhydride (MN)/80 methylene dianiline (MDA):20 thiodianiline (TDA)/pyromellitic dianhydride (PMDA)	1000
P105A[c]	NA/80MDA:20TDA/BTDA	1050
P11BA[d]	NA/80MPD:20TDA/BTDA	1100
None	NA/70MPD:30TDA/BTDA	1100

(a) This system was selected during earlier studies under Contract NAS1-9532 as the key ingredient in adhesive formulations for press-bonding (Reference 1).

(b) This system was identified in Contract NAS3-13489 as an improved thermally stable autoclave processable A-type resin system (Reference 3).

(c) This system was identified in Contract F33615-70-C-1392 as being suited ideally to autoclave molding of boron monofilament and graphite fiber reinforced composites (Reference 2)

(d) Because use of TDA had successfully induced autoclave processability to resin formulations in the preceding two cases (Reference 2 and 3) and since P11B had provided excellent strengths in press-bonded joints (Reference 1), it was decided to evaluate a TDA modified P11B.

TABLE IV.

PRELIMINARY RESIN SCREENING STUDIES

RESIN[a] SYSTEM	Bonding Process			
	Press Cycle		Simulated Autoclave Cycle	
	Shear Strength, psi		Shear Strength, psi	
	at R.T.	at 600°F	at R.T.	at 600°F
1100 FMW NA/MPD/BTDA	3013	2080	2480	1880
1000 FMW MN/80MDA:20TDA/PMDA	2560	1830	2733	1750
1050 FMW NA/80MDA:20TDA/BTDA	3200	1940	2770	1920
1100 FMW NA/80MPD:20TDA/BTDA	2850	1970	2390	1900
1100 FMW NA/70MPD:30TDA/BTDA	2730	2060	1970	1790

(a) Key to Resin Formulas:

NA = Nadic anhydride

MN = Methyl nadic anhydride

MPD = *meta*-phenylene diamine

MDA = Methylene dianiline

BTDA = Benzophenone tetracarboxylic acid dianhydride

PMDA = Pyromellitic dianhydride

TDA = Thio-dianiline

These data showed that a decrease in the ratio of the selected diamine to TDA (mixed diamine segment of the polymer) from the 80:20 proportions defined in Reference 2 and 3 to 70:30 actually decreased the shear strength of bonded assemblies. Subsequently, the 70:30 system was eliminated from further evaluations.

In order to define more clearly the A-type polyimide resin to be used throughout the autoclave bonding studies, it then was decided that additional elevated temperature aging data should be generated. Lap shear specimens were aged in an air circulating oven at 600°F with a hot air velocity of

250 ft/min and an air change rate of 400 ft^3/min. Aging at 600°F showed that all systems were degraded but those containing MPD/TDA had better thermal stability than systems containing MDA/TDA as the diamine.

The percent strength retention shown in Table V follows closely the data presented in Table VI of Reference 1. A summary of strength retention on the earlier work is provided for comparison in Table VI of this report. The data presented here in Table VI also substantiates that a MPD:TDA combination is one of the better systems.

A noticable decrease in bondline thickness was observed (See Table V) in conjunction with the deterioration in shear strength for 600°F aged specimens. This leads one to suspect that polymer shrinkage contributes to the deterioration in shear strength values through increased residual stresses.

The combined results of these studies as presented in Tables IV and V provided the required information for selection of one system for use throughout the balance of this program. It was observed from these results that the long-term thermal stability of systems containing MPD was better than that of systems containing MDA. Neither substitution of MN for NA nor PMDA for BTDA offered any improvement in properties. Also, it was shown quite clearly that the use of mixed diamine systems containing TDA provided autoclave processability to the systems. This finding concurs with the conclusions drawn from the work reported in References 2 and 3. Therefore, the P11BA resin system was selected as the A-type polyimide portion of the adhesive primer and paste compounds throughout this program.

TABLE V.

EFFECT OF 600°F AGING ON LAP SHEAR STRENGTH OF CANDIDATE AUTOCLAVABLE ADHESIVE SYSTEMS

RESIN[a] SYSTEM	R.T. LAP SHEAR PROPERTIES					
	Initially		After 288 Hours @ 600°F			
	Bond Line Thickness Inch	Shear Strength Ksi	Bond Line Thickness Inch	Shear Strength Ksi	Strength Retention %	Bondline Shrinkage %
1100 FMW NA/MPD/BTDA	0.0086[b]	3.72	0.0085	2.04	54.8	1
1000 FMW MN/80MDA: 20TDA/PMDA	0.0050	3.08	0.0032	1.53	49.7	36
1050 FMW NA/80MDA: 20TDA/BTDA	0.0058	2.56	0.0038	1.26	46.9	35
1100 FMW NA/80MPD: 20TDA/BTDA	0.0051	3.36	0.0037	1.76	52.4	29

(a) See Table IV.

(b) Adhesive was supported on Style 104/A 1100 glass scrim for this system only.

TABLE VI.

SUMMARY FOR TASK III EVALUATION OF LAP-SHEAR SPECIMENS[b]

RESIN[a] SYSTEM	Room Temperature Shear Strength Of Unaged Specimens Ksi	Room Temperature Shear Strength Of Specimens Aged 300 Hours At 600°F Ksi	Strength Retention %
NA/90MPD:10TDA/BTDA 1100 FMW	1.66	0.88	56
NA/90MDA:10TDA/BTDA 1050 FMW	2.31	0.78	34
NA/MPD/BTDA 1100 FMW	2.18	1.05	48
NA/MDA/PMDA 1100 FMW	1.03	0.43	42
NA/90MDA:10TDA/PMDA 1000 FMW	1.79	0.82	46
NA/MDA/BTDA 1150 FMW	1.89	0.81	43

(a) See Table IV.
(b) See Reference 1.

4. PROCESS DEVELOPMENT STUDIES

Secondary bonding autoclave processes were developed and evaluated for preparing assemblies consisting of graphite fiber reinforced composite panels to titanium alloy and all titanium alloy assemblies. Following these studies, a process for autoclave molding primary bonded structures consisting of graphite fiber reinforced polyimide and titanium alloy assemblies was developed. These studies are discussed in detail throughout the following narrative.

Prior to development of finalized bonding processes, procedures for chemical milling titanium alloy and polyimide composite bonded assemblies were established which provided for close scrutiny of the adhesive interface. The initial studies utilized glass fabric reinforced composites as one substrate which provided flat bonded assemblies. After the chemical milling procedures were established, similar assemblies were fabricated utilizing graphite fiber reinforced composites as one substrate, but these were bowed upon cooling to room temperature. Removal of the titanium alloy face from both the glass and graphite fiber reinforced composites revealed in the

majority of panels the desired homogeneous adhesive interfaces with no apparent cracks, porosity nor voids. Because visual examination of the adhesive interface did not provide a sufficiently discrimatory screening method between variations in bonding processes, a mechanical test method was adopted. Several test methods were evaluated but finally standard lap-shear tests were utilized using metal to metal adherends. Detailed discussion of the evaluation and development efforts for screening test methods are provided in Appendix C.

4.1 MIXED SUBSTRATE SECONDARY BONDING PROCESS DEVELOPMENT

Screening of variations in autoclave processing conditions were performed using the etched titanium visual examination and lap shear test methods described in Appendix C. These studies defined the most promising drying cycle after which further studies to optimize the bonding process were carried out using the short beam shear test method (See Appendix C). Mixed substrate specimens failed in the composite at low stress levels when the adhesive, A-type polyimide resin (P11BA) was used as the resin matrix for the composites. Consequently, a brief screening of press-molded A-type polyimide graphite composites was performed which indicated that P13N resin provided higher shear strengths in press-molded composites than the P11BA adhesive resin. Details of these studies are provided below.

4.1.1 Process Screening Studies

Prepregs were prepared consisting of Courtaulds HTS graphite fiber tows (8 tows per inch) and P13N polyimide resin. These were cut and plied with one transverse ply sandwiched between two longitudinal plies and press-molded under 300 psig pressure for 60 minutes at 550°F. The composite panels were cut into 6-inch squares and lightly abraded with 320 grit silicon carbide paper.

Pieces of 6Al-4V titanium alloy sheet, 0.062-inch thick by 6-inch square were prepared for bonding by vapor degreasing and grit blasting with 50 micron alumina. They then were immersed in Pasa-Jel 107 for 15 minutes at 70°F, water rinsed and dried at 150°F. All strips were primed within two hours of preparation with autoclavable Primer P4 (Appendix B). Autoclavable Adhesive Film A5F (Appendix B) was applied to one faying surface and then the unmated primed surfaces and adhesive film were dried in

an air circulating oven after which the faying surfaces were mated. Four layers of Style 181 glass fabric were layed upon an aluminum alloy base plate and the assembly was placed on top (See Figure 4). Four layers of one-inch wide Style 181 glass fabric were placed around the periphery of the assembly over which was placed four layers of Style 181 glass fabric. A vacuum bag was fabricated in accordance with Figure 4 and this assembly was installed in an autoclave. Air was evacuated out of the bag to approximately 15 psia, nitrogen gas pressure was applied and the assembly was heated to 600°F at a rate of 10°F/minute. After curing at 600°F for 60 minutes the assembly was cooled down to room temperature in the vacuum bag (approximately 15 psia pressure).

The bonded assemblies were coated with a chemical milling mask (Turco S145) and dried for 30 minutes at 200°F. A "window" then was cut through the mask to expose the titanium alloy face. This assembly was immersed in hydrofluoric acid (16% w/w) for 30 minutes to etch away the exposed titanium alloy. Gentle agitation of the acid was maintained throughout the etching process. Upon completion of this operation the specimens were washed thoroughly in water and the remainder of the mask was stripped off.

The adhesive interface was dark-grey after removal from the hydrofluoric acid but light rubbing with steel wool produced a shiny aluminum colored surface provided by the aluminum powder filler in the adhesive and primer. Visual examination of the adhesive surface revealed no cracks, voids nor porosity in all but the assemblies prepared by drying for 15 minutes at 275°F only. These assemblies, as shown in Figure 5, resulted in a deteriorated adhesive bondline after etching which it is assumed resulted from a porous bondline. All other adhesive interfaces had excellent appearance as may be observed in Figure 5.

Screening of variations in drying/imidizing cycles and applied pressures are reported in Table VII. These results show that the combination of 15 minutes at 275°F plus 5 minutes at 350°F with 100 psig bonding pressure provided the highest shear strengths, at both room temperature and at 600°F. However, before making the final selection of a bonding process, further screening and optimization studies using short beam shear specimens were performed as planned.

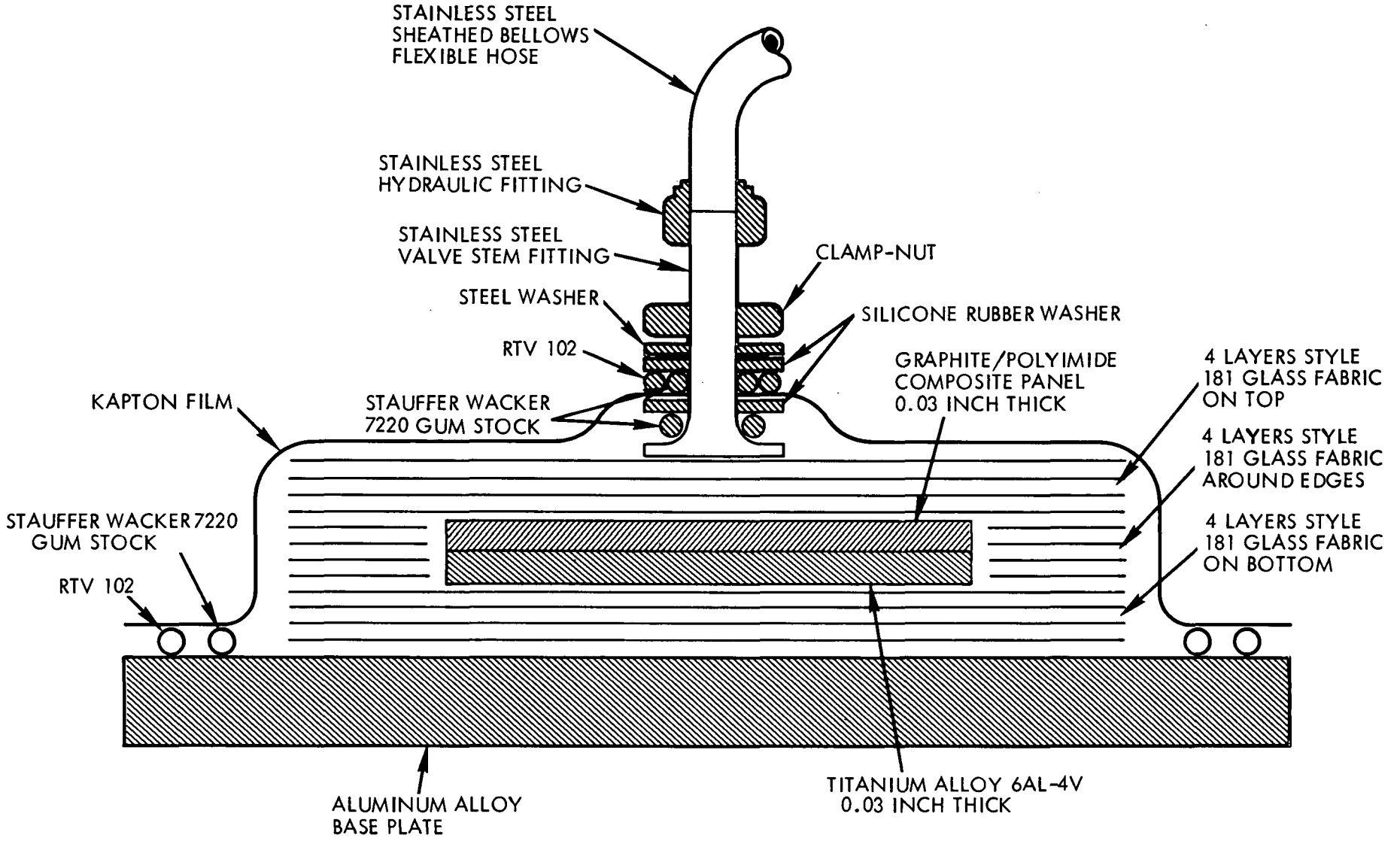
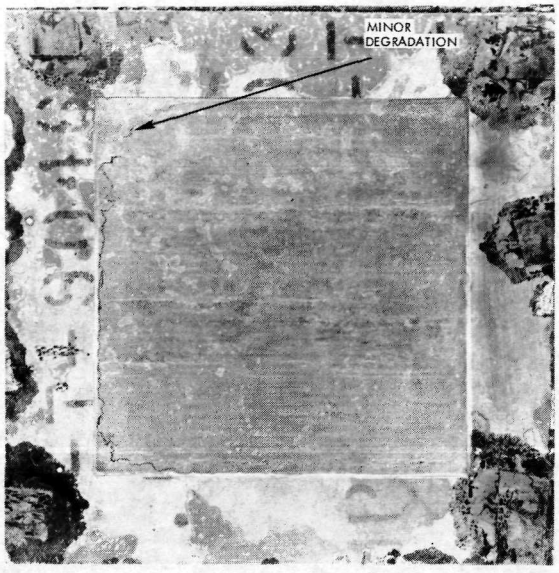
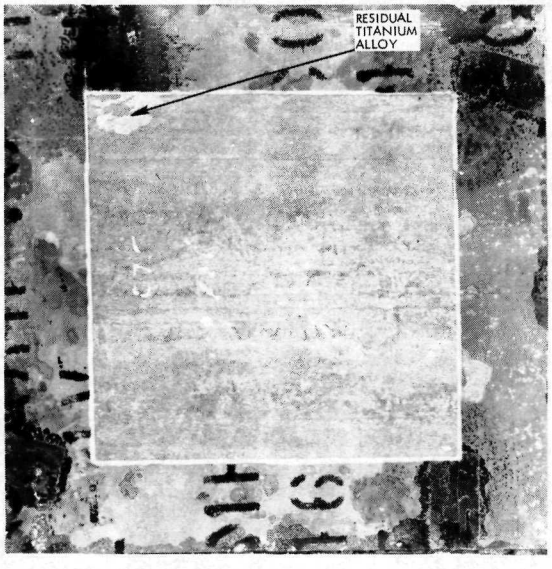


Figure 4. Vacuum Bag Schematic

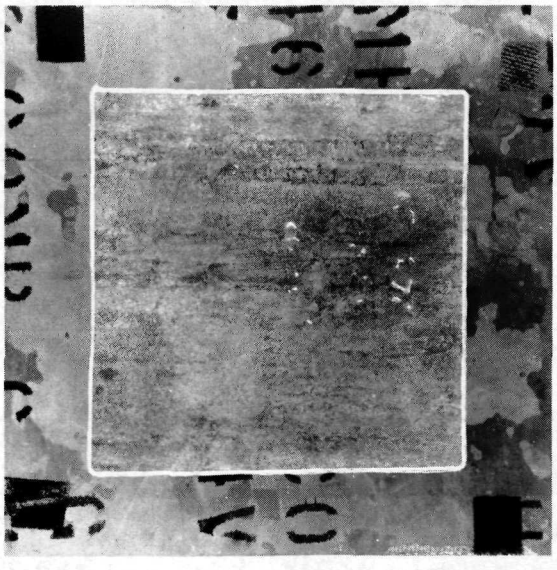
15 Mins, 275°F, 100 psig



15 Mins, 275°F, 200 psig



15 Mins, 275°F, plus
5 Mins, 350°F, 100 psig



15 Mins, 275°F, plus
5 Mins, 350°F, 200 psig

Figure 5. Chemical Milled Titanium Alloy Graphite Composite Specimens

4.1.2 Process Optimization Studies

Process optimization studies for preparing secondary bonded, mixed substrate specimens in an autoclave were performed. During these studies short beam shear specimens (used for screening various processes) were prepared using 0.25-inch wide by 0.062-inch thick strips of titanium alloy 6Al-4V and unidirectional graphite fiber reinforced composites (See Section 4.1.3). The assemblies were prepared and bonded similarly to the six-inch square panels except the cold nine-cavity mold (See Figure 6) was used and the bagging system conformed to the schematic shown in Figure 7.

TABLE VII.
PROCESS SCREENING

Drying Cycle Min/°F	Applied Pressure psig	Adhesive[a] Examination	Lap Shear Strength[b] Ksi at	
			R.T.	600°F
15/275	100	Highly Degraded	2.98	2.24
15/275	200	Minor Degradation	3.33	1.95
15/275 5/350	100	No voids, nor porosity	3.41	2.34
15/275 5/350	200	No voids, nor porosity	2.97	1.87

(a) Examination of titanium alloy to graphite composite adhesive interface after chemical milling the titanium alloy.

(b) Titanium alloy 6Al-4V.

Bonded specimens containing P11BA resin matrix composites failed at very low stress levels when tested by the short beam shear test method. All failures occurred in the composite and the stress levels corresponded with the composites strength (See Tables VIII and IX) obtained during the studies discussed in Section 4.1.3.

All specimens containing P13N resin matrix composites provided good shear strengths (See Table VIII). The 100 psig bonding pressure appeared to provide higher properties than the 200 psig bonding pressure and post-cure of these specimens appeared to increase the shear strength (values up to 20 Ksi were obtained). It was concluded from these studies that a 100 psig bonding pressure plus a post-cure of 16 hours at 550°F is the most promising

bonding cycle for secondary bonded mixed substrate specimens. Therefore, these steps were incorporated into the secondary bonding process throughout this program.

4.1.3 Press Molded Composites Screeening

Prepreg tapes were prepared by drum winding Courtaulds HTS graphite fiber tows at 8 tows per inch. These tows were impregnated by spray gun with either P11BA or P13N resin. Molding of composites from these prepregs proceded by stacking 0.25-inch wide strips of prepreg to sixteen plies thickness in the cold nine-cavity mold (See Figure 6). The mold was placed open into an air circulating oven and the prepreg was staged in accordance with Table IX. After this cycle, the hot mold was assembled and placed into a press preheated to 600°F. Immediately, pressure was applied to the mold until it was fully closed to stops whereupon the composites were cured under pressure for one hour. Shear strengths of the resultant composites were determined by the short beam method using a 4:1 span to depth ratio. These tests (See Table IX) clearly indicated that the P13N resin matrix composites provided the highest shear strength of the two resins evaluated for press molding.

TABLE VIII.

SHORT BEAM SHEAR SECONDARY BONDING PROCESS SCREENING

SUBSTRATES	BONDING PRESSURE psig	BEFORE POST-CURE		AFTER POST-CURE	
		Strength Ksi	Type of Failure	Strength Ksi	Type of Failure
Titanium to Titanium	200	16.3	Cohesive	17.8	Cohesive
	100	16.9	Cohesive	16.1	Cohesive
Titanium to P11BA Graphite Composite	200	7.1	Composite	7.8	Composite
	100	7.5	Composite	6.6	Composite
Titanium to P13N Graphite Composite	200	12.8	Cohesive	(a)	(a)
	100	16.0	Cohesive	16.2	Tensile in Composite

(a) Not performed because the specimens bonded under 100 psi pressure were obviously superior.

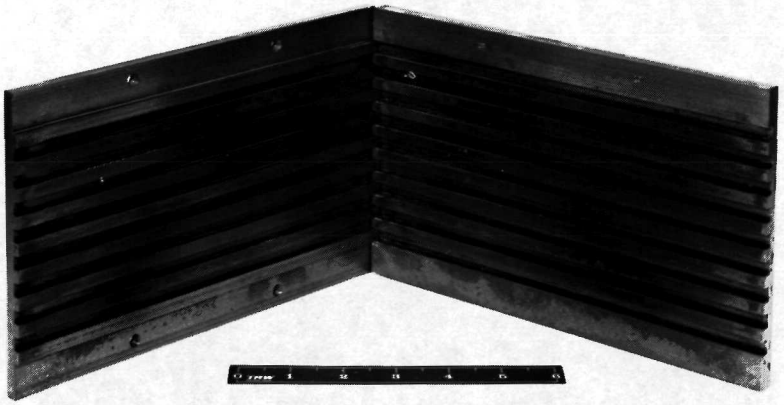
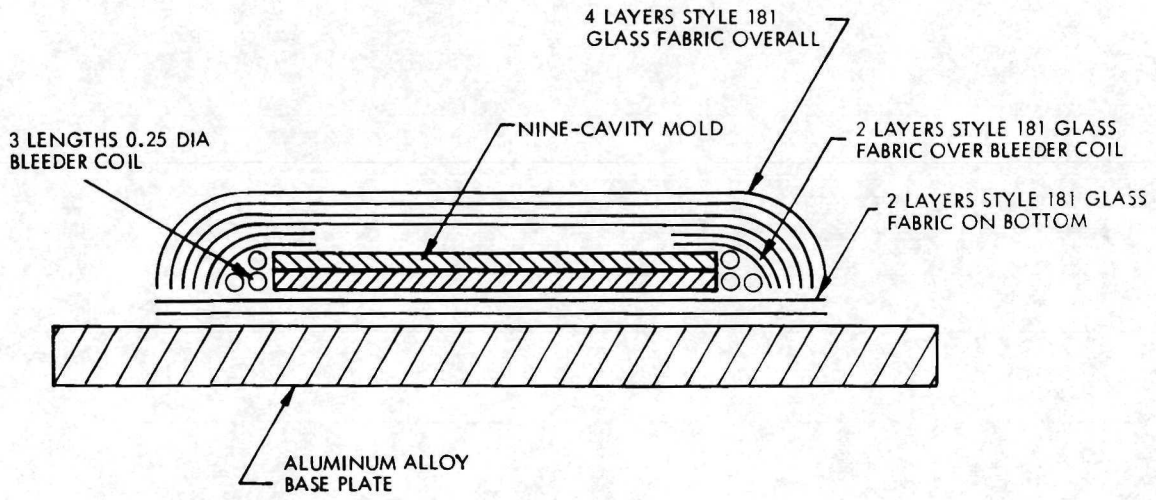


Figure 6. Photograph of the Nine-Cavity Mold



(a) See Figure 5 for vacuum fitting assembly schematic.

Figure 7. Schematic of Nine-Cavity Mold Vacuum Bag[(a)] Assembly

TABLE IX.

PRESS-MOLDED GRAPHITE COMPOSITE SCREENING

Resin System	Pre-Staging Cycle	Shear[(a)] Strength Ksi	Resin Content % w/w
P11BA	2 hrs. @ 250°F	3.2	40.8
P11BA	2 hrs. @ 250°F 2 hrs. @ 400°F	7.8	42.5
P13N	2 hrs. @ 400°F	12.3	39.1

(a) Short beam shear 4:1 span to depth ratio.

4.2 AUTOCLAVE BONDING OF SINGLE SUBSTRATE SPECIMENS

Single substrate short beam specimens were bonded by a similar process to the mixed substrate bonding process. From the short beam shear strengths shown in Table VIII there did not appear to be any significant difference between the processes evaluated. The bond strengths obtained during these evaluations were equivalent to those obtained by the press bonding process (Reference 1). Therefore, it was concluded that the same secondary bonding process was suitable for both mixed and single substrate specimens.

4.3 PRIMARY BONDING PROCESS DEVELOPMENT

Process development studies were performed for preparing primary bonded specimens consisting of Courtaulds HTS graphite fiber tows impregnated with P11BA polyimide resin and titanium alloy 6Al-4V. Processing parameters evaluated were:

- Three molding pressures
- Autoclave molding cycle developed under Contract F33615-70-C-1392 (Reference 2) (Process A)
- Autoclave molding cycle developed for secondary bonding (Process B)

Details of these evaluations are provided in the following discussion.

4.3.1 Preparation of Specimens

Prepreg tapes consisting of P11BA amide-acid varnish and Courtaulds HTS high strength graphite fiber tows were drum-wound by the process defined in

Appendix D-1. These tapes then were processed as detailed in 4.3.1.1 for Process A and in 4.3.1.2 for Process B.

4.3.1.1 Process A - After removal from the drum the tapes were dried for ten minutes in a 200°F air circulating oven. These tapes were cut into 0.25-inch wide by 9.0-inch long strips and stacked unidirectionally eight ply thick in the cold nine-cavity mold (Figure 6). The mold was placed open into an air circulating oven and the prepreg was staged for 50 minutes at 220°F, 30 minutes at 250°F and two hours at 275°F.

Strips of 6Al-4V titanium alloy sheet, 0.062-inch thick by 0.250-inch wide were prepared for bonding by vapor degreasing and grit blasting with 50 micron alumina. They then were immersed in Pasa-Jel 107 for 15 minutes at 70°F, water rinsed and dried at 150°F. All strips were primed within two hours of preparation with autoclavable Primer P4. The primer was applied thinly by brush, autoclavable Adhesive Film A5F was applied to one faying surface and then the unmated primed surfaces and adhesive film were dried in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F. These primed and adhesively coated strips were placed on top of the staged prepreg in the nine-cavity mold (Reference 6) and the upper part of the mold was installed. The assembly was placed in a vacuum bag and installed in an autoclave as described in Appendix D. Part temperature was raised to 275°F at a rate of 3 to 4°F per minute at which time nitrogen gas pressure was applied and the heat-up rate was changed to 10 to 12°F per minute up to 575°F. The assemblies were cured for 60 minutes and then cooled in the vacuum bag (approximately 15 psia) down to room temperature. After removal from the mold, all specimens were post-cured for 16 hours at 550°F in air.

4.3.1.2 Process B - After removal from the drum, the tapes were dried in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F (the same drying cycle used for Adhesive Film A5F). The resultant prepregs had very little tack at room temperature but were very flexible. Moderate heating and pressure induced sufficient tack to afford consolidation of these prepregs. These tapes were cut into 0.25-inch wide by 9.0-inch long strips and stacked unidirectionally eight-ply thick in the cold nine-cavity mold (Figure 6).

Strips of 6Al-4V titanium alloy sheet, 0.062-inch thick by 0.250-inch wide were prepared for bonding by vapor degreasing and grit blasting with 50 micron alumina. They then were immersed in Pasa-Jel 107 for 15 minutes at 70°F, water rinsed and dried at 150°F. All strips were primed within two hours of preparation with autoclavable Primer P4. The primer was applied thinly by brush, autoclavable Adhesive Film A5F was applied to one faying surface and then the unmated primed surfaces and adhesive film were dried in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F. These primed and adhesively coated strips were placed on top of the prepreg in the nine-cavity mold (Figure 6) and the upper part of the mold was installed.

The assembly was placed in a vacuum bag (See Figure 7) and installed in an autoclave. Air was evacuated out of the bag out of the bag (approximately 15 psia) and a nitrogen gas pressure of 100 psig was applied. The assembly was heated to 575°F at the rate of 10°F/minute where it was cured for 60 minutes after which it was cooled in the vacuum bag (15 psia approximately) down to room temperature. These bonded strips were post-cured for 16 hours at 550°F in air.

4.3.2 Evaluation of Specimens

Primary bonded assemblies molded under the processing conditions defined in Table X were machined into 0.650-inch long specimens and tested for shear strength by the short beam method. During these tests, the specimens were supported on the ends at a 4:1 span to depth ratio and loaded at the mid-point with the titanium face in compression. After failure, the composite portion was removed from the titanium portion of the specimen and resin content was determined. Properties of the specimens molded under the four different conditions are provided in Table X. The specimens molded under 50 psig pressure failed catostrophically in the composites whereas the other specimens had simple shear failures in the composites. The specimens molded by Process B under 100 psig pressure failed at an average shear stress of 13.58 Ksi which is 14% higher than obtained by Process A. Consequently, this process was selected for preparing primary bonded assemblies for detailed evaluation studies.

TABLE X.

PRIMARY BONDING AUTOCLAVE PROCESS STUDIES

Autoclave[a] Molding Process	Molding Pressure psig	Average Shear Strength Ksi	Composite[b] Resin Content % w/w
A	200	7.74	35.5
A	100	11.92	39.0
A	50	11.41	36.4
B	100	13.58	30.9

(a) A - Process developed under Contract F33615-70-C-1392 (Reference 2).
B - Process developed for secondary bonding assemblies.

(b) PIBA/Courtaulds HTS Graphite Fiber

5. DETAILED EVALUATION OF AUTOCLAVE PROCESSED, BONDED STRUCTURES

Lap shear and short beam shear specimens were prepared by the procedures described in Appendix D-5 and D-6 using Primer P4 and Adhesive Film A5F. These were prepared in sufficient quantities to provide NASA Langley Research Center with one hundred secondary bonded, titanium alloy and graphite composite short beam specimens and twenty-five lap shear specimens as well as specimens for the detailed evaluations performed by TRW Systems. Discussion of the evaluations performed by TRW Systems is provided in the following section.

5.1 LAP-SHEAR STRENGTH EVALUATION

Eleven lap shear panels (55 test coupons) were autoclave-bonded by the process described in Appendix D-5 from which twenty-five coupons were selected randomly for room temperature testing. The average value obtained from these tests was 3.4 Ksi (See Table XI) which is higher than the average obtained earlier for press-bonded panels (See Figure 2). Scatter between the twenty-five values obtained was small, *i.e.*, fifty percent of the values were within the range of 3.4 Ksi to 3.5 Ksi (See Figure 8) whereas only thirty-two percent of the values for press-bonded specimens were within the same range. The 3.4 Ksi shear strength value is approximately thirty percent higher than

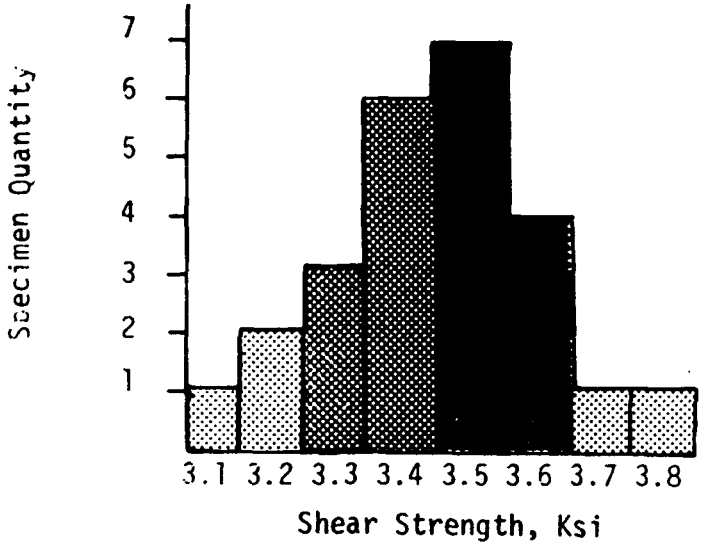
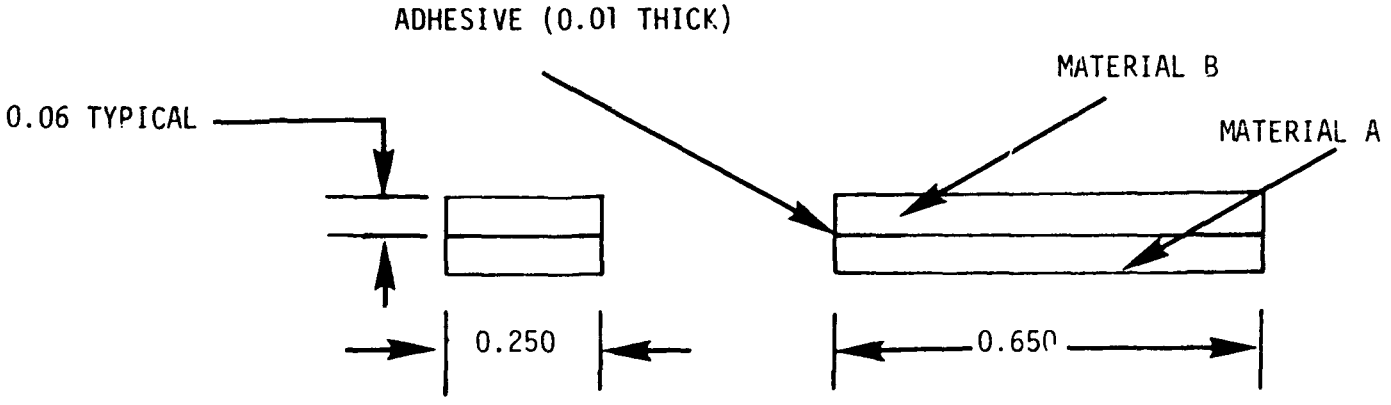


Figure 8 . Shear Strength Property Distribution - Autoclave Bonded Specimens



(a)

Figure 9 . Short-Beam Shear Specimen

(a) All dimensions in inches.

values reported for commercially available high temperature adhesive systems (Reference 4).

Five test coupons then were selected randomly for elevated temperature testing (600°F). These evaluations provided an average shear strength value of 1.8 Ksi at 600°F which is equal to the value reported for other polyimide resin adhesives at 500°F (Reference 4) and higher than that reported specifically for FM34 and AF-A-2009 at 600°F (Reference 5). It is apparent therefore, that the 1.8 Ksi shear strength at 600°F obtained during this program is superior to that obtainable from other polyimide adhesives.

5.2 ROOM TEMPERATURE SHORT BEAM TESTS

Short beam shear specimens were machined to the dimensions defined in Figure 9 from assemblies bonded in accordance with Appendix D-6. These specimens were tested in flexure using a single point loading with two support points four times the total specimen thickness apart (0.5-inch approximately). Loading rate was 0.05-inch per minute.

Three autoclave batches of all titanium alloy specimens were bonded from which three specimens were tested from each batch. The average value for all nine specimens was 16.2 Ksi (See Table XII) and the average value scatter between batches was within ten percent (See Table XIII). It was shown in Reference 1 that compressive yielding of the titanium alloy occurs when the calculated bondline stress exceeds 17 Ksi. This value was exceeded only in two cases although all specimens approached the yield point for titanium alloy immediately prior to adhesive failure.

Secondary bonded specimens containing titanium alloy and P13N graphite fiber composite substrates were tested similarly. These specimens failed in shear within the graphite composite. The values obtained (See Table XII) were higher than the values obtained during the press-molded composites screening studies (See Table IX). Since the modulii of titanium alloy 6Al-4V and the P13N/Courtaulds HTS graphite fiber composites are approximately the same ($\sim$16.0 X10^6 psi), the two substrate materials were considered to be structurally identical. Consequently, the calculation of the stress at bondline previously necessary for boron composite and titanium alloy specimens (Reference 1) was not applicable.

TABLE XI.

LAP-SHEAR STRENGTH[a]

PROPERTY	VALUE
SHEAR STRENGTH AT 70°F	
Average, Ksi [b]	3.4
Standard Deviation, Ksi	0.2
SHEAR STRENGTH AT 600°F	
Average, Ksi [c]	1.8
Standard Deviation, Ksi	0.1
STRENGTH RETENTION AT 600°F, %	52
BONDLINE THICKNESS, INCH	0.0084 to 0.0090

(a) Titanium alloy 6Al-4V, 0.050-inch thick, 1.0-inch wide, 0.5-inch overlap.

(b) Average of twenty-five specimens.

(c) Average of five specimens

TABLE XII.

SHORT BEAM TESTS AT 70°F

ADHERENDS		SHEAR STRENGTH, Ksi	
Material A	Material B	Average Value	Standard Deviation
Titanium	Titanium	16.2[a]	1.4
Graphite Composite	Titanium	13.6[b] [c]	0.4
Graphite Prepreg Primary Bond	Titanium	13.8[b] [c]	0.6

(a) Average of nine specimens

(b) Average of five specimens

(c) Shear failure in the composite

TABLE XIII.

QUALITY CONTROL TESTS FOR

SECONDARY BONDED SINGLE SUBSTRATE SPECIMENS

Autoclave Batch	Average[a] Calculated Shear Strength, Ksi	Standard Deviation, Ksi
A	15.9	1.9
B	15.5	0.3
C	17.0	1.5
Average[b]	16.2	1.4[c]

(a) Average of three specimens

(b) Average of nine specimens (3 from each batch).

(c) Collective standard deviation.

Evaluation of primary bonded short beam specimens consisting of titanium alloy 6Al-4V and P11BA resin reinforced with Courtaulds HTS graphite fibers provided an average shear strength of 13.8 Ksi. These specimens failed in shear within the graphite composite similarly to the secondary-bonded specimens but at a slightly higher shear stress. This value is the highest shear strength obtained by TRW Systems for autoclave-molded A-type polyimide resin composites reinforced with Courtaulds HTS graphite fiber (Reference 2).

5.3 ELEVATED TEMPERATURE SHORT BEAM TESTS

Short beam shear specimens were tested at 600°F after 30 minutes soak at 600°F by the same test method used for the room temperature evaluations.

The all titanium alloy secondary bonded specimens provided an average value of 10.9 Ksi for the 600°F shear strength (See Table XIV). This value is below the calculated shear stress level at which yielding of the titanium alloy occurs (11.5 Ksi at 600°F). It is assumed, therefore, that the calculated value of 68% for strength retention of the adhesive at 600°F is valid.

Shear strength at 600°F average values for secondary bonded and primary bonded titanium alloy to graphite composite were 10.1 Ksi and 10.9 Ksi respectively (See Table XIV). These specimens failed in shear within the composite and therefore, the strength retention values provided in Table XIV can be regarded also as composite shear strength retention values. The seventy-eight percent shear strength retention shown for the primary bonded specimens is higher than obtained previously for autoclave molded composites (forty-three percent reported in Reference 2).

5.4 LOW TEMPERATURE SHORT BEAM TESTS

Low temperature mechanical property tests were performed on short beam shear specimens using the same method employed previously for room temperature and 600°F testing. The specimens were soaked for 30 minutes prior to loading at -65°F. Failure in all titanium alloy specimens occurred at an average calculated shear stress of 30.2 Ksi. Yielding at -65°F of titanium alloy 6Al-4V occurs at a calculated shear stress value of 19.1 Ksi (obtained using the same formula presented in Reference 1 where the compressive modulus at -65°F of titanium alloy 6Al-4V is 16.5 X 10^6 psi). The 30.2 Ksi value therefore must be corrected down to 19.1 Ksi (Reference Table XV).

TABLE XIV.

SHORT BEAM TESTS AT 600°F

ADHERENDS		SHEAR STRENGTH, Ksi		STRENGTH[a] RETENTION %
Material A	Material B	Average[b] Value	Standard Deviation	
Titanium	Titanium	10.9	0.3	68
Graphite Composite	Titanium	10.1[c]	0.5	63
Graphite Prepreg Primary Bond	Titanium	10.9[c]	0.5	78

(a) $\frac{\text{Strength at 600°F}}{\text{Strength at 70°F}}$ X 100

(b) Average of five specimens

(c) Shear failure in the composite.

TABLE XV.

SHORT BEAM TESTS AT -65°F

ADHERENDS		SHEAR STRENGTH, Ksi		STRENGTH[a] RETENTION %
Material A	Material B	Average[b] Value	Standard Deviation	
Titanium	Titanium	30.2[d]	2.9	200
Graphite Composite	Titanium	14.5[c]	1.7	107
Graphite Prepreg Primary Bond	Titanium	18.2[c]	0.7	132

(a) $\frac{\text{Strength at } -65°F}{\text{Strength at } 70°F} \times 100$

(b) Average of five specimens

(c) Shear failure in the composite.

(d) Compressive yield of Titanium Alloy ~19.1 Ksi.

Secondary bonded P13N graphite composite and titanium alloy specimens failed in shear in the composite at an average shear stress of 14.5 Ksi. The primary bonded P11BA graphite composite and titanium alloy specimens also failed in the composite but at a much higher shear stress (18.2 Ksi). Although none of the primary bonded specimen's calculated shear strength exceeded 19.1 Ksi, most of the specimens were loaded at the point of failure to a stress level approaching the -65°F yield point of the titanium alloy.

All of these values exceeded those obtained previously during the press-bonding studies (Reference 1) and property scatter, as indicated by the standard deviation values, was particularly low for the primary bonded specimens (within 3.3%).

5.5 HIGH TEMPERATURE AGING TESTS

Short beam shear specimens were aged in a 600°F air circulating oven with a horizontal air velocity of 250 feet/minute and an air change rate of 400 cubic feet/minute. Bondlines were parallel to the air flow. Specimens were withdrawn after 200, 500 and 1000 hours of aging; room temperature short beam shear strengths were determined as shown in Table XVI.

The all titanium alloy specimens after all three aging durations provided calculated shear strengths above 17.2 Ksi. Since these values were above the shear stress level at which the titanium alloy yields, the calculated shear strength values must be corrected down. It is apparent from these results that the A5F adhesive is not degraded after long-term aging at 600°F when protected from the air environment.

The P13N graphite composites in the secondary bonded specimens had degraded badly after 200 hours of exposure and failed in composite shear at 7.1 Ksi. After 500 hours the specimens had degraded so severely that they were not suitable for test.

Primary bonded specimens were degraded slightly after 500 hours of exposure but still provided a composite shear strength of 11.6 Ksi. This value is 86% of the initial room temperature shear strength.

5.6 LOW TEMPERATURE AGING TESTS

Specimens were aged at -65°F in a Conrad-Missimer test chamber cooled with refrigerated circulating air and were withdrawn after periods of 200, 500 and 1000 hours and tested at room temperature (Table XVII).

TABLE XVI.
AGING STUDIES AT 600°F

TABLE XVI.
AGING STUDIES AT 600°F

Type of Specimens	Hours of Aging at 600°F	Measured Weight Change, %	Shear Strength, Ksi		Strength Retention, %
			Average Value	Standard Deviation	
Ti/Ti (Secondary Bond)	200	-0.21	18.0	1.5	124
	500	-0.4	21.5	1.2	140
	1000	-0.34	21.1	1.4	137
Ti/Graphite (Secondary Bond)	200	-1.45	7.1 (c)	2.6	52
	500	-4.92	(b)	(b)	(b)
	1000	-7.00	(b)	(b)	(b)
Ti/Graphite Prepreg (Primary Bond)	200	-2.58	10.4	0.3	
	500	-4.77	11.6 (c)	0.5	86
	1000	-6.90	(b)	(b)	(b)

(a) Average of five specimens tested at room temperature using a single point flexural loading at 4:1 span to depth ratio.

(b) Graphite composite was grossly degraded and therefore was not suitable for test.

(c) Shear failure within the composite.

TABLE XVII.

AGING STUDIES AT -65°F

Type of Specimens	Hours of Aging at -65°F	Measured Weight Change, %	Shear Strength, Ksi[a]		Strength Retention, %
			Average Value	Standard Deviation	
Ti/Ti (Secondary Bond)	200	+0.025	24.5	1.3	150
	500	+0.012	24.1	1.5	150
	1000	+0.050	22.4	1.0	138
Ti/Graphite Composite (Secondary Bond)	200	+0.015	8.9 [c]	0.6	65
	500	+0.011	9.2 [c]	0.6	68
	1000	+0.033	14.6[b][c]	3.7	108
Ti/Graphite Prepreg (Primary Bond)	200	+0.025	16.9 [c]	1.2	123
	500	+0.049	12.6 [c]	3.5	93
	1000	+0.032	18.0 [c]	1.3	130

(a) Average of five specimens tested at room temperature using a single point flexural loading at 4:1 span to depth ratio except as noted in (b) below.

(b) Average of two specimens.

(c) Shear failure within the composite.

The all titanium alloy specimens all failed at a calculated shear stress above the shear stress at which the titanium alloy yields. Therefore, it is apparent that the -65°F aging did not degrade the adhesive since these values must be regarded as the same as the initial room temperature shear strength values.

The P13N graphite composites in the secondary bonded specimens failed after 200 and 500 hours aging at lower shear stress than obtained initially. However, after 1000 hours of aging they provided calculated shear strengths above the initial values. It is believed that these values are the result of scatter between batches of specimens rather than an aging phenomenon. Therefore, it is assumed that these results show that long-term aging at -65°F does not affect the shear strength of secondary bonded P13N graphite composite and titanium alloy specimens.

Primary bonded P11BA graphite composite and titanium alloy specimens provided higher calculated shear strength values than obtained initially after 200 and 1000 hour aging durations. The values for the specimens aged for 1000 hours were above the calculated shear stress value at which the

titanium alloy yields therefore, these must be corrected down. After 500 hours of aging, the specimens provided an average value slightly lower than the initial values although this is attributed to property scatter between batches of specimens. It is apparent therefore, that long-term aging at -65°F does not degrade these primary bonded specimens.

5.7 STRESS RUPTURE TESTS

Stress rupture tests were performed in 600°F circulating air by the same method used previously (Reference 1). By this method, triplicate short beam shear specimens were loaded at the desired stress level with a dead weight and lever arm mechanism (See Figure 10 and Figure 11). Time to rupture was monitored by measuring the specimens deflection while under load both by visual measurement and autographically recording the time at which the specimen's previously determined deflection-at-failure at 600°F was exceeded.

Secondary bonded P13N graphite composite and titanium alloy specimens loaded at 75% shear stress level at 600°F failed after 234 hours (See Table XVIII). This time-to-rupture was higher than obtained previously with the P13N boron composite and titanium alloy specimens (Reference 1). These earlier

TABLE XVIII.
STRESS RUPTURE TESTS AT 600°F

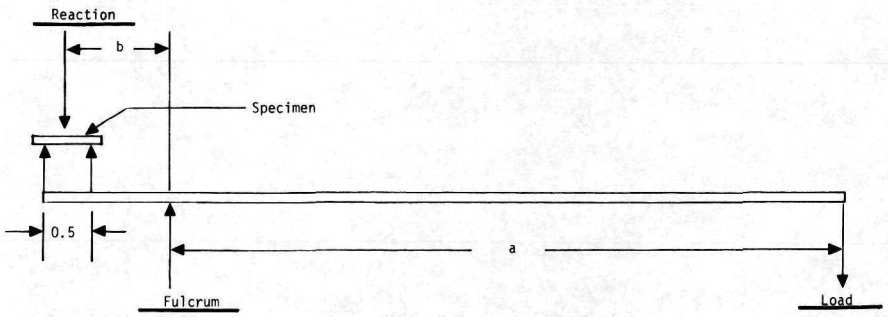
ADHERENDS		STRESS[a] LEVEL, %	STRESS LOADING, Ksi	AVERAGE TIME TO FAILURE, HOURS
Material A	Material B			
Graphite Composite	Titanium	75	7.6	234[b]
		46	5.1	670[b]
Titanium	Titanium	75	8.2	90[c]
		50	5.5	600
		25	2.7	690[d]

(a) Average of three specimens.

(b) Excessive degradation in composite necessitated test termination.

(c) Very high deflection occurred prior to adhesive failure (0.125-inch approximately).

(d) Test stopped prior to specimen failure because of equipment malfunction.



Lever Arm Ratios (1)

Jig	a : b Ratio
1	6.8 : 1
2	6.5 : 1
3	6.9 : 1

(1) Test jigs were callibrated using load cells at the reaction point and dead weight loads.

Figure 10. Schematic of Test Fixture

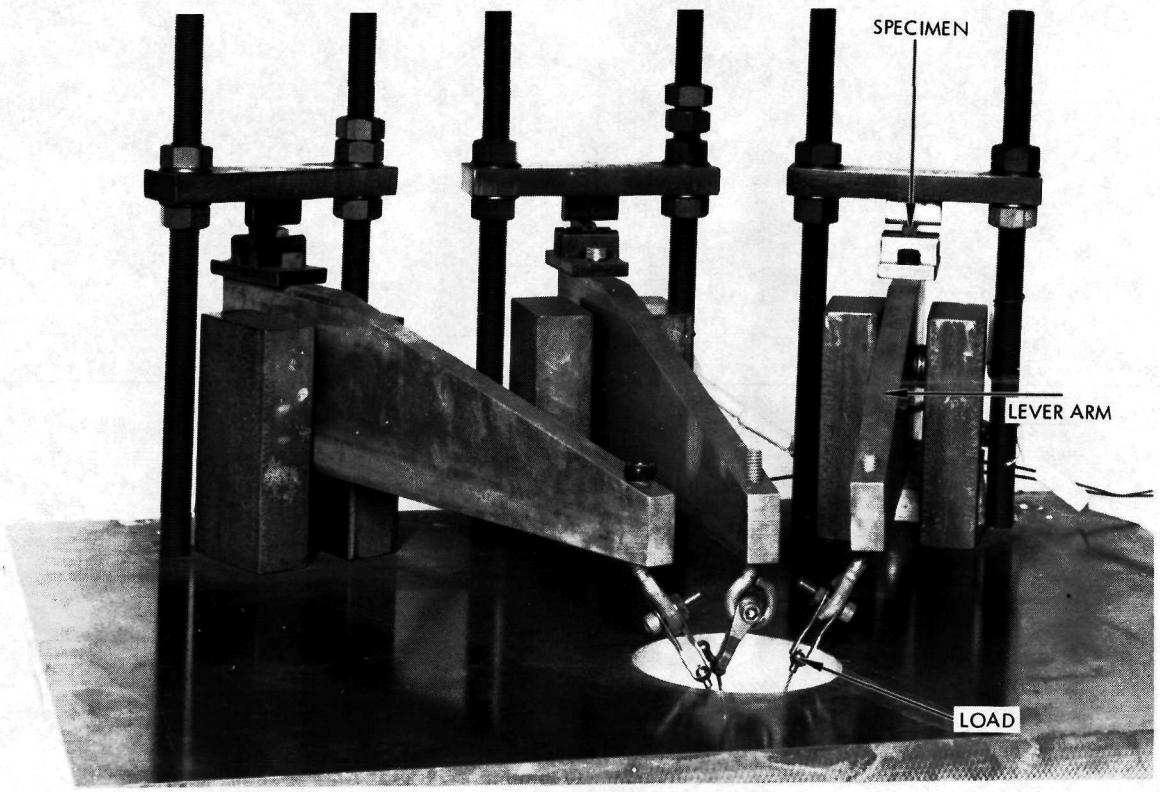


Figure 11. Stress Rupture Test Jig

75% stress level tests provided a time-to-rupture of 94 hours which indicates an improvement during the recent evaluation of 160%. Similar specimens stressed at 46% shear stress level survived 670 hours of test but the P13N graphite composites had degraded so severely that the test was stopped.

It then was agreed mutually between the NASA Langley Research Center and TRW Systems Program Managers to employ all titanium alloy secondary bonded specimens instead of the mixed substrate specimens. At 75% shear stress level these specimens deflected approximately 0.125-inch prior to failure. This deflection indicates that a creep problem was encountered although the specimens survived 90 hours of test which is identical to the time-to-rupture obtained previously for the P13N boron composite and titanium alloy specimens. These single substrate specimens failed after 600 hours when loaded at 50% shear stress which was twice as long as obtained on the previous program. Specimens were loaded at 25% shear stress level but at 690 hours after test commencement an equipment malfunction occurred. The temperature in the test chamber exceeded 1000°F resulting in severe distortion of both the aluminum alloy lever arms and the base plate of the stress rupture jig. Examination of the test specimens after removal from the jig did not produce any evidence of adhesive failure. All stress rupture tests were terminated at this point.

Time-to-rupture for the specimens tested during this phase and during the earlier phase of the program were plotted and are presented in Figure 12. These plots show a slower rate of shear strength deterioration for the autoclave bonded specimens than for the press bonded specimens.

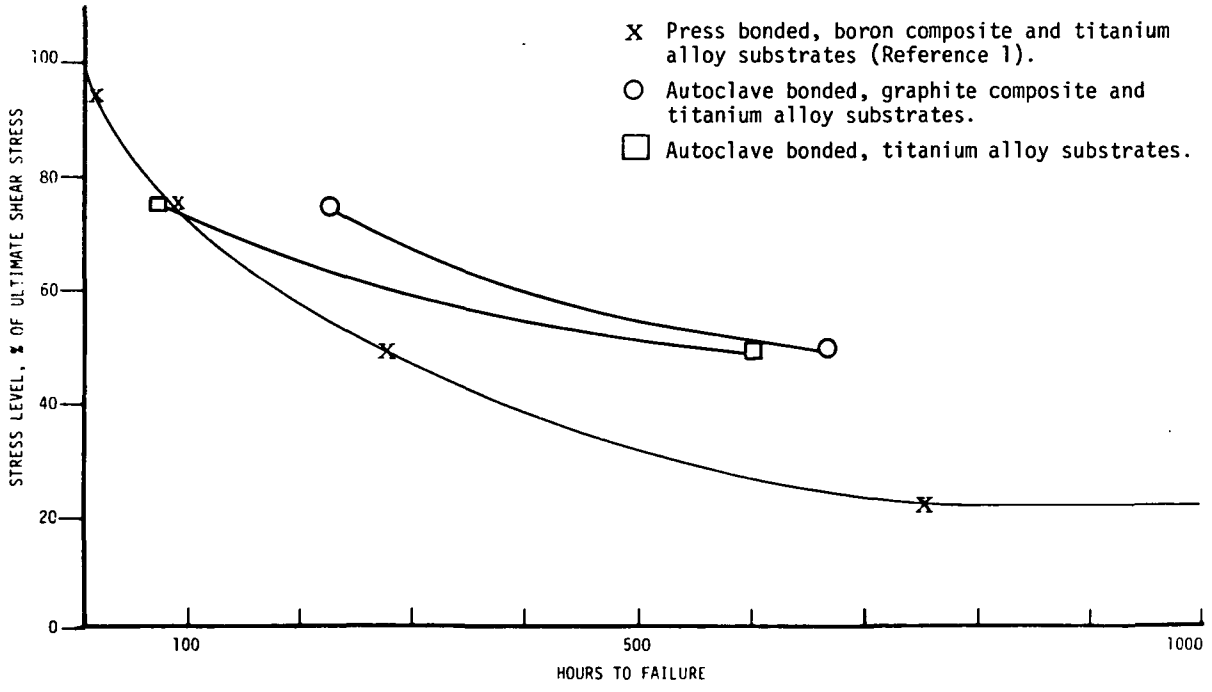


Figure 12. Stress Rupture Tests At 600°F

6. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to formulate autoclave processable thermally stable adhesives and to develop autoclave bonding processes for graphite composite and titanium alloy structures. Based on these findings, recommendations are given for further material and process improvement studies.

6.1 CONCLUSIONS

1. The adhesive system developed during the first phase of this Contract (Reference 1) was modified by replacing the single diamine A-type polyimide formulation used previously (P11B) with a formulation containing a mixture of TDA and MPD (P11BA). This modification provides the desired autoclave processability to the new adhesive system.

2. The new adhesive system provided higher lap shear strengths at room temperature and 600°F with titanium alloy substrates than reported previously with other high temperature adhesive systems, *e.g.*, FM 34 and AF-A-2009 (Reference 4 and 5).

3. The modified A-type resin formulation (P11BA) provided higher composite shear strengths at room temperature and 600°F than obtained previously by TRW Systems with the same reinforcement (Courtaulds HTS graphite fiber, Reference 2).

4. Long-term aging at 600°F and -65°F of all titanium alloy bonded specimens did not degrade the shear strength measurably, therefore, it was concluded that the adhesive is excellent for long-term 600°F and -65°F service.

5. The calculated shear stress in all titanium alloy secondary bonded short beam specimens exceeded the shear stress at which the titanium alloy yields in compression. Secondary and primary bonded graphite composite/titanium alloy specimens failed in shear within the composites. Therefore, it was concluded that the limiting factor in most of the short beam shear specimens was either the compressive yield strength of the titanium alloy or the short beam shear strength of the graphite composites.

6. Secondary bonded assemblies consisting of titanium alloy and graphite composite with a bond area of thirty-six square inches displayed no voids or cracks when subjected to detailed examination of the exposed adhesive face after removal of the titanium alloy face by etching. Therefore, it was concluded that this adhesive is suited ideally for the preparation of large surface area bonded joints by autoclave processing.

7. A vacuum-bagging system for autoclave bonding and molding was developed using commercially available materials that survive the 575°F cure cycle necessary for curing the autoclave processable A-type polyimide resin.

6.2 RECOMMENDATIONS

1. Modifications to the polymers in this adhesive system in order to obtain long-term serviceability at temperatures above 600°F (*e.g.*, 700°F to 800°F) are warranted in order to meet current industry needs.

2. Evaluation of this adhesive and development of processes for bonding honeycomb sandwich assemblies is warranted in order to extend the scope of applicability for this system.

3. Detailed structural tests are warranted in order to obtain detailed engineering design data for autoclave bonded joints that will permit the design of sophisticated flight structures.

4. Detailed shelf-life stability and batch reproducibility studies are warranted in order to establish manufacturing limits for scaled-up applications of this system.

5. TRW Systems has shown during preliminary company funded studies that the autoclavable adhesive system developed under this contract is suited for weld-bonding titanium alloy substrates. Spot welds were formed with the uncured adhesive film between the substrates after which the adhesive was cured in an oven without pressure application. Further studies are warranted to optimize the spot-welding process and to generate engineering data.

7. NEW TECHNOLOGY

New autoclave processable adhesive compound formulations were developed based upon the technology established during the first phase of the program (Reference 1). A-type polyimide resin composition was identified as being the most suitable of the resin formulations evaluated for application in autoclave processable, thermally stable adhesive compounds. This composition (P11BA) consisted of nadic anhydride, *meta*-phenylene diamine, thio-dianiline, and benzophenone tetracarboxylic acid dianhydride. The combination of P11BA and Amoco AI-1137 resins as a copolymeric blend together with aluminum powder filler and Cab-O-Sil thixotropic agent provided autoclave bonded joints possessing high shear strengths and excellent thermal stability. An additional feature of the P11BA resin was the excellent shear strength obtained from autoclave molded, Courtaulds HTS graphite fiber reinforced, P11BA composites.

APPENDIX A.

PREPARATION OF A-TYPE POLYIMIDE VARNISHES

The following procedure was used to prepare 1100 FMW NA/80 MPD:20 SDA/BTDA (P11BA) and is representative for all A-type polyimide varnishes prepared and utilized in this program.

The following quantity of ingredients were mixed as described below to produce a 40% solids varnish:

meta-Phenylenediamine (MPD)	170.00 g
4,4'-diaminodiphenyl sulfide (TDA)	67.93 g
Nadic anhydride (NA)	233.40 g
Benzophenone tetracarboxylic acid dianhydride (BTDA)	378.67 g
	850.00 g solids
Dimethyl formamide (DMF)	1275 g

The MPD and TDA were dissolved in 400 ml of DMF in a round bottomed flask fitted with a stirring apparatus and a nitrogen gas bleed. A slurry of NA in 252 ml of DMF was slowly added (with stirring) to the diamine mixture while controlling the solution temperature between 20°C and 25°C. After the last addition of the NA slurry, stirring was continued for ten minutes, then a slurry of BTDA in 700 ml of DMF was added until all ingredients were combined in a temperature of 20°C to 25°C. The material was stirred for two hours and then allowed to stand for 30 minutes under a nitrogen purge. The one-half gallon of varnish was prepared at a 40% solids loading which was transferred to screw cap bottles and stored under nitrogen until used for fabrication.

APPENDIX B.

PREPARATION OF ADHESIVE FORMULATIONS

The adhesive formulations were prepared using the constituents defined in Table B-1 by the following process.

> The A-type polyimide and Amoco AI-1137 amide-acid varnishes first were blended together. Aluminum powder then was added and blended in together with Cab-O-Sil for adhesive paste. The primer compounds then were diluted with DMF. Adhesive film was prepared by immersing Style 104 A-1100 glass scrim in the adhesive paste and then drawing the impregnated scrim through wiper bars to provide a 32% w/w adhesive coating. The resultant films were dried for 5 minutes at 275°F.

TABLE B-1

ADHESIVE/PRIMER FORMULATIONS

CONSTITUENTS[a]	PARTS BY WEIGHT OF CONSTITUENTS IN ADHESIVE/PRIMER FORMULATIONS			
	P2	P4	A1F[c]	A5F
P11B (Resin Solids)	50	---	50	---
P11BA (Resin Solids)	---	50	---	50
AI1137 (Resin Solids)	50	50	50	50
Aluminum Powder, Grade 101	100	100	175	175
Cab-O-Sil	---	---	5	5
DMF	400	400	150	150
Glass Scrim	---	---	(b)	(b)

(a) P11B — 1100 FMW NA/MPD/BTDA
P11BA — TRW A-type polyimide, 1100 FMW NA/80MPD: 20 TDA/BTDA
AI1137 — Amoco Corporation
Aluminum Powder — Aluminum Company of America, Grade 101
Cab-O-Sil — Cabot Corporation
DMF — Dimethyl formamide, Baker Reagent Grade
Glass Scrim — Style 104 glass scrim, A1100 amino-silane coupling agent

(b) One layer of scrim coated with adhesive paste to provide a 32% w/w. resin solids content. Film dried for 5 minutes at 275°F.

(c) Designated A1P when used as a paste without glass scrim.

APPENDIX C.

DEVELOPMENT OF ADHESIVE SCREENING METHODS

A preliminary method was established to examine bondlines of titanium alloy bonded specimens whereby the titanium alloy was etched away in a solution of hydrofluoric acid allowing visual examination of the interfacial adhesive film. The unsupported adhesive film between the two titanium adherends appeared to have very few voids and was not affected by the hydrofluoric acid.

Subsequently, a 6-inch by 6-inch assembly of titanium alloy and glass fabric reinforced polyimide composite was bonded using the simulated autoclave process. This panel was prepared as follows:

> Style 181-E glass fabric reinforced, PI3N polyimide resin laminates, 0.030-inch thick, were cut into 6 X 6-inch square panels. These were lightly sanded on one face and solvent washed. Titanium alloy 6Al-4V panels, 6 X 6-inch square and 0.03-inch thick, were sandblasted (320 grit alumina) and treated by immersion in Pasa-Jel 107 for 15 minutes. The titanium alloy faying faces then were coated with Primer P4 and dried for 15 minutes at 275°F. Adhesive Film A5F was applied to one of the open faying surfaces, and then both the primer coating and the adhesive film were imidized by treating open-face in an air circulating oven for 5 minutes at 350°F.
>
> The faying surfaces were mated, placed upon an aluminum alloy base plate and then vacuum bagged in an autoclave in accordance with the schematic shown in Figure 4 of the text. Air was evacuated down to provide 15 psia pressure and 200 psig nitrogen gas pressure was applied. The assembly was heated to 600°F at a rate of 10°F per minute and cured at 600°F for 60 minutes. Cooling of the assemblies was performed in the vacuum bag (approximately 15 psia pressure) down to room temperature (70°F).

The resultant bonded assembly was flat and of good general appearance. This assembly then was coated with a chemical milling mask (Turco S145) and dried for 30 minutes at 200°F. A "window" was cut through the mask to expose the titanium alloy face. This assembly was immersed in hydrofluoric acid (16% w/w) for 30 minutes to etch away the exposed titanium

alloy. Gentle agitation of the acid was maintained throughout the etching process. Upon completion of this operation, the specimens were washed thoroughly in water and the remainder of the mask was stripped off.

The adhesive interface was dark-grey after removal from the hydrofluoric acid but light rubbing with steel wool produced a shiny aluminum colored surface provided by the aluminum powder filler in the adhesive and primer. Microscopic examination of the adhesive surface revealed no cracks, voids or porosity.

A second bonded assembly then was prepared using a graphite reinforced composite panel in place of the glass fabric laminate. This assembly was bowed severely upon completion of cure but removal of the titanium alloy surface again revealed a homogeneous, void-free adhesive surface.

It then was apparent that visual exmainations of exposed adhesive surfaces did not provide a sufficient means of discriminating between panels because both autoclave bonded panels had good appearance, *i.e.*, microscopic examinations revealed no cracks, nor porosity. Consequently, alternative means of screening panels were investigated.

The first approach investigated consisted of cutting one-inch wide strips from the six-inch square panels and then slotting them to form notched lap shear test coupons (see Figure C-1). When tested at room temperature, these panels provided particularly low shear strengths (1290 psi). These low properties were attributed to high peel loading resulting from the severely bowed condition of the test coupons. Since the bowing was assumed to be caused by high residual stresses resulting from the large differences in thermal expansion at 600°F of the two substrates (titanium alloy and graphite composite), it was decided to investigate testing at 600°F. This approach assumed that since the panels were bonded at 600°F, the 600°F test temperature would stress relieve the specimens and form flat panels. The results from these evaluations again were unsatisfactory since sporadic values ranging from 200 psi to 990 psi were obtained.

A second screening method then was evaluated. This method employed fabricating standard single lap shear specimens using mixed substrates

of titanium alloy and graphite composites. These specimens were fabricated using 0.06-inch thick by six-inch square unidirectional graphite composite panels which were secondary bonded to standard five-finger titanium alloy lap shear coupons. A standard half-inch wide overlap bonded joint was formed. These were tested at room temperature and yielded low values of 1100 psi. Failures occurred in the graphite composites and appeared to result either from high peel loads or from uneven stressing of the fibers.

It was obvious that in order to evalute mixed substrates by lap shear testing, double lap shear specimens would be necessary. However, since this would necessitate fabricating special bonding fixtures for the autoclave which were outside the scope of the program, it was decided to forego this screening method. Instead, metal to metal single lap shear specimens (Figure C-2) were bonded in a bonding jig (Figure C-3) simultaneously under the same pressure bag with six-inch square mixed substrate panels. Using this approach, evaluation of the parameters being screened was made based upon adhesive interface appearance and upon titanium/titanium lap shear strength.

Short beam shear tests were performed on specimens conforming to Figure 9 using a standard single point flexural loading at a 4:1 span to depth ratio.

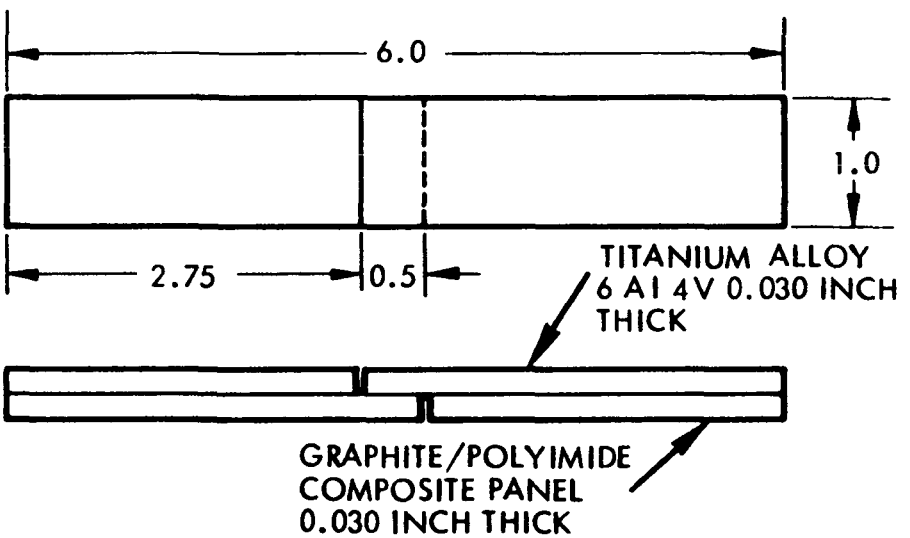


Figure C-1. Slotted Lap Shear Specimens

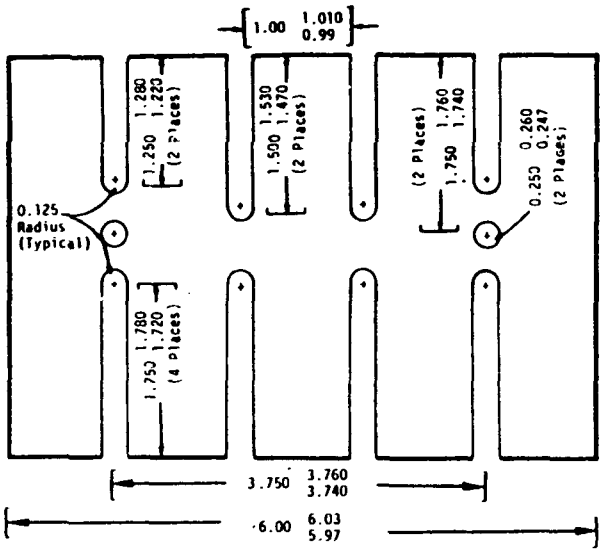


Figure C-2. Lap Shear Finger Panel

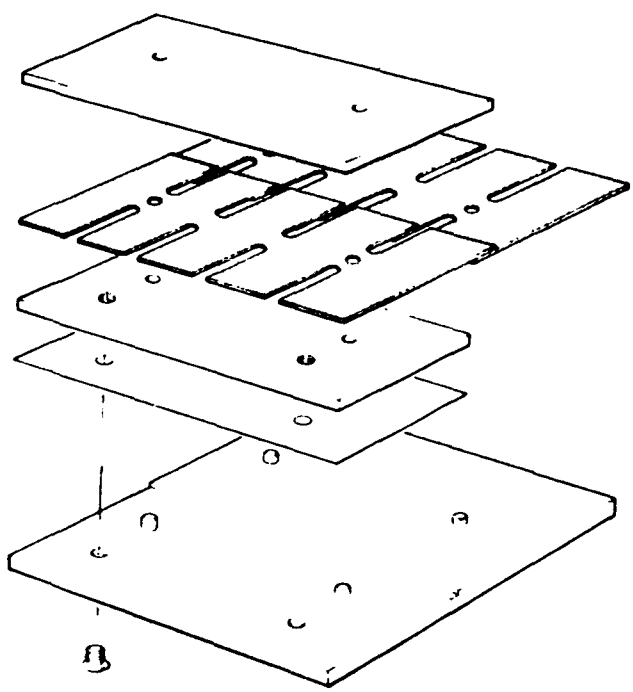


Figure C-3. Lap Shear Bonding Jig

APPENDIX D.

DETAILED PROCESSING PROCEDURES

D.1 PREPARATION OF P13N AND P11BA/HTS PREPREG TAPE

Step 1. Lay Mylar film (0.002-inch thick) onto the 30-inch diameter drum of the TRW drum winder. Tape in place with double back masking tape.

Step 2. Collimate Courtaulds HTS high strength graphite fiber tows (10,000 fibers per tow) at approximately 25-feet per minute to provide 8 tows per inch of width. Spray P11BA or P13N amide-acid varnish onto the graphite fibers using a Binks Model 62, Nozzle 66SD, to provide a spray fan of approximately 1-inch width. Pot pressure to be 3 to 5 psig.

Step 3. Control resin content in the prepreg tapes by premeasuring the quantity of varnish to be applied. After completion of the graphite winding operation, the residual varnish from the above premeasured quantity is to be applied evenly to the collimated tows by the spray gun during subsequent passes of the traversing head.

Step 4. Partially dry the impregnated tapes for 30 minutes using infrared heating lamps positioned approximately 10-inches from the rotating drum surface.

Step 5. Remove tapes from the drum supported on the Mylar backing film.

D.2 PREPARATION OF TITANIUM ALLOY 6Al-4V FOR BONDING

Step 1. Vapor degrease the titanium alloy faying surfaces.

Step 2. Grit blast the faying surfaces with 50 micron alumina and water rinse.

Step 3. Immerse grit blasted surfaces in Pasa-Jel 107 for 15 minutes at 70°F.

Step 4. Rinse in distilled water and air dry at 150°F.

Step 5. Apply primer thinly by brush within two hours of Pasa-Jel treatment.

Step 6. Thermally treat primed surfaces in an air circulating oven for 15 minutes at 275°F and 5 minutes at 350°F.

D.3 PREPARATION OF PRESS MOLDED COMPOSITES

Step 1. Stack P13N/HTS prepreg tape (See D.1) to the desired thickness in a cold mold.

Step 2. Place mold open into an air circulating oven for two hours at 400°F.

Step 3. Assemble mold and place into a press preheated to 600°F.

Step 4. Immediately apply pressure until the mold is closed to stops.

Step 5. Cure under pressure for one hour.

D.4 PREPARATION OF PRESS BONDED LAP SHEAR SPECIMENS

Step 1. Prepare titanium alloy 6Al-4V lap shear panels (Figure C-2) for bonding cleaning and priming with Adhesive Primer P2 in accordance with D.2.

Step 2. Lay Adhesive Film A1F onto one of the mating surfaces.

Step 3. Thermally treat adhesive film and primed surfaces in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F.

Step 4. Assemble panels in a bonding jig (Figure C-3).

Step 5. Load into press preheated to 600°F and apply 100 psig pressure.

Step 6. Cure for 60 minutes under pressure.

Step 7. Post cure specimens in an air circulating oven for 16 hours at 550°F.

D.5 PREPARATION OF AUTOCLAVE BONDED LAP SHEAR SPECIMENS

Step 1. Prepare titanium alloy 6Al-4V lap shear panels (Figure C-2) for bonding, cleaning and priming with Adhesive Primer P2 in accordance with D.2.

Step 2. Lay Adhesive Film A5F onto one of the mating surfaces.

Step 3. Thermally treat adhesive film and primed surfaces in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F.

Step 4. Assemble panels in a bonding jig (Figure C-3).

Step 5. Prepare vacuum bag assembly in accordance with Figure 7 of the text.

Step 6. Install assembly in an autoclave.

Step 7. Evacuate air out of the vacuum bag to provide a pressure of 15 psia.

Step 8. Apply 100 psig nitrogen gas pressure.

Step 9. Heat assembly to 575°F at the rate of 10°F per minute.

Step 10. Cure for 60 minutes under pressure.

Step 11. Release pressure and cool the assembly down to room temperature in the vacuum bag (15 psia approximately).

Step 12. Remove lap shear specimens and post cure in an air circulating oven for 16 hours at 550°F.

D.6 PREPARATION OF SECONDARY BONDED SHORT BEAM SPECIMENS BY AUTOCLAVE PROCESSING

Step 1. Prepare titanium alloy 6Al-4V strips, 0.062-inch thick by 0.250-inch wide, for bonding by cleaning and by priming with Adhesive Primer P4 both in accordance with D.2.

Step 2. Prepare P13N/HTS composite strips, 0.062-inch thick (8 ply) by 0.250-inch wide for bonding by lightly abrading with 320 grit silicon carbide paper.

Step 3. Lay Adhesive Film A5F onto one of the mating surfaces.

Step 4. Thermally treat adhesive film and primed surfaces in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F.

Step 5. Assemble strips into a cold 9-cavity mold (Figure 6 of the text).

Step 6. Prepare vacuum bag assembly per Figure 4 of the text.

Step 7. Install assembly in an autoclave.

Step 8. Evacuate air out of the vacuum bag to provide a pressure of 15 psia.

Step 9. Apply 100 psig nitrogen gas pressure.

Step 10. Heat assembly to 575°F at the rate of 10°F per minute.

Step 11. Cure under pressure for 60 minutes.

Step 12. Release pressure and cool to room temperature in the vacuum bag (15 psia approximately).

Step 13. Remove bonded strips and post cure for 16 hours at 550°F in an air circulating oven.

D.7 PREPARATION OF PRIMARY BONDED SHORT BEAM SPECIMENS BY AUTOCLAVE PROCESSING

Step 1. Prepare P11BA/HTS prepreg tapes in accordance with D.1.

Step 2. Thermally treat prepreg in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F.

Step 3. Cut tapes into 0.25-inch wide by 9.0-inch long strips.

Step 4. Stack prepreg strips 8-ply thick in a cold 9-cavity mold (Figure 6 of the text).

Step 5. Prepare titanium alloy 6Al-4V strips, 0.062-inch thick by 0.250-inch wide, for bonding by cleaning and priming with Adhesive Primer P4 in accordance with D.2.

Step 6. Apply Adhesive Film A5F to the primed surface and thermally treat in an air circulating oven for 15 minutes at 275°F plus 5 minutes at 350°F.

Step 7. Place primed and adhesively coated strips on top of the prepreg in the 9-cavity mold.

Step 8. Install upper part of the mold and prepare vacuum bag assembly in accordance with Figure 7 of the text.

Step 9. Install assembly in an autoclave.

Step 10. Evacuate air out of the vacuum bag to provide a pressure of 15 psia.

Step 11. Apply nitrogen gas pressure of 100 psig.

Step 12. Heat assembly to 575°F at the rate of 10°F per minute.

Step 13. Cure under pressure for 60 minutes.

Step 14. Release pressure and cool assembly in the vacuum bag (15 psia approximately) down to room temperature.

Step 15. Remove strips and post cure for 16 hours at 550°F in an air circulating oven.

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ABSTRACT

THE DEVELOPMENT OF AUTOCLAVE PROCESSABLE, THERMALLY STABLE ADHESIVES FOR TITANIUM ALLOY AND GRAPHITE COMPOSITE STRUCTURES

By

R. W. Vaughan and R. J. Jones

This Final Report describes the work performed during the second phase of this program where autoclave processable, thermally stable adhesives for titanium alloy and graphite composite structures were developed. The A-type polyimide adhesive resin P11B developed during the first phase of this program was modified by use of mixed diamines (thio-dianiline and *meta* phenylene diamine) which provided the desired autoclave processability. This new resin was termed P11BA. It was shown that copolymeric blends of P11BA and Amoco AI-1137 amide-imide resin provided improved adhesive properties when autoclave processed over the properties obtained previously by press bonding with P11B based copolymeric blended adhesives. Properties of bonded assemblies are presented for long-term aging at both elevated and low temperatures, and also stress-rupture tests at elevated temperature.